Upgrading effluent from anaerobic digestion of dairy manure through hydrothermal carbonization

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INTRODUCTION

- Anaerobic digestion (AD) has been widely used to produce biogas from biowaste. Its post-AD water-rich residues, also known as AD effluent, typically is ordorous, very hard to dewater, and may contribute to greenhouse gas emissions[1]. Waste minimization of AD effluent is a great challenge nowadays.
- **Hydrothermal carbonization (HTC)** is an attractive waste management strategy for biomass residuals, especially, for those with high water content (>20%)[2].
- Solid product from HTC, termed as **hydrochar**, has high calorific value close to that of coal[3], high chemical and thermal stability, moderately high surface area and adsorption capacity[4].

AIM

- Using AD effluent as raw material, evaluate mass and energy characteristics of hydrochar, and optimize parameters for the HTC process.
- Investigate the feasibility of integrating HTC after AD to gain an efficient energy use of AD effluent.

METHODS

- **AD effluent** (abbreviated as ADE): Collected from an AD digester using manure as feedstocks in a dairy farm of Ohio, USA, with TS 7.26% and original pH 7.50, marked as ADE-O, was stored at 4°C prior to use.
- **pH adjustment**: To look into the influence of pH to HTC, pH was adjusted to 6.00 with concentrated sulfuric acid and marked as ADE-A.
- HTC experiments were conducted in a 1-L stirred pressure reactor (Parr USA).
- Three parameters were investigated for HTC process:
  - Temperature (T: 180, 220 and 260°C).
  - Reaction time (t: 30, 50 and 70 min).
  - pH (ADE-O and ADE-A).
- **Central composite design (CCD)** and response surface methodology (RSM) were applied for the optimization of hydrochar production. **ANOVA** at p-value of 0.05 was used for model analysis.
- Procedure of experiments is depicted in Fig. 1.

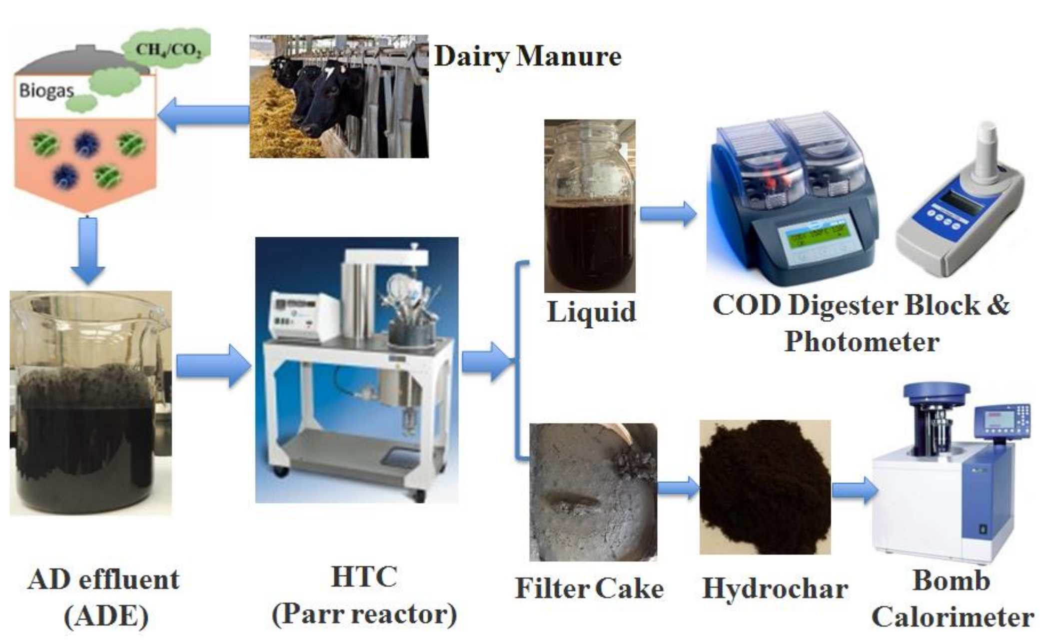

Fig 1. *Procedure for HTC and the following analysis*

- **Calorific value**: (in MJ/kg, higher heating value，HHV) HHV of dried AD effluent and hydrochar was determined by bomb calorimeter (C2000 basic, IKA).
- **COD** (Chemical Oxygen Demand) (mg/L): ADE and liquid from HTC were digested in COD digester block and then analyzed by COD Photometer (HACH).
- **Outputs analyzed:**
  - Mass balance of HTC process (dry matter distribution among hydrochar, liquid and gas).
  - Hydrochar yield ($M_{db,hydrochar}$/ $M_{db,ADE}$).
  - Energy yield ($M_{db,hydrochar}$*$HHV_{hydrochar}$)/($M_{db,ADE}$*HHV_{ADE}).
  - Calorific value (HHV) of the hydrochar.
  - COD ratio of HTC processed water（total COD in liquid after HTC/total COD in ADE）

*note: M_{db}: dry based mass

RESULTS AND DISCUSSIONS

Visual assessment of hydrochar

Typical hydrochar samples are shown in Fig. 2.

- Compared with original ADE, hydrochar could be easily ground by pestle and mortal.
- Judging from the ease and speed of filtration, and also the water hold capacity of hydrochar, hydrochar at higher T appeared to be more hydrophobic.
- When T ≥ 260°C, hydrochar was darker and particles were more homogeneous and compacted.

Fig 2. *Samples of hydrochar*

Mass balance of HTC process

- Mass distributions among hydrochar, liquid and gas (=dry matter of raw ADE- hydrochar- liquid) are shown in Fig. 3.
- Compared with ADE-O, the addition of acid improved the degradation of effluent, thus less solid hydrochar and more dry matter in gas were achieved from ADE-A.

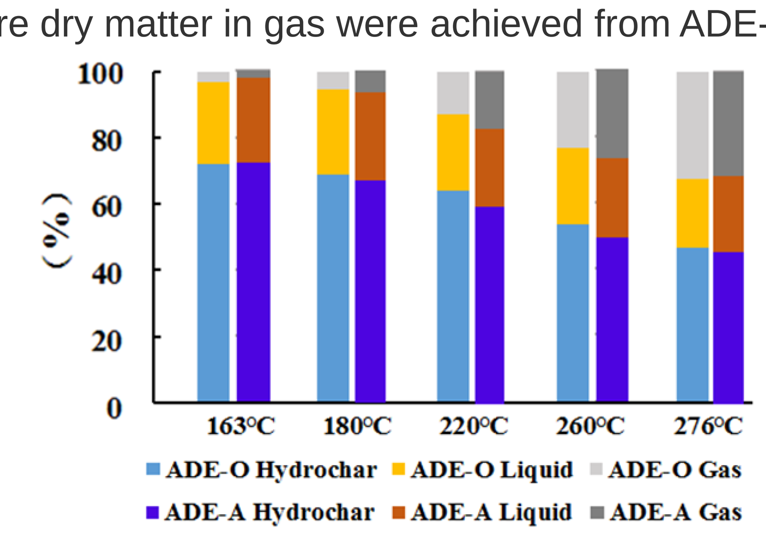

Fig 3. *Mass balance of different HTC Process*

Hydrochar yield

- Temperature (T) and pH (ADE-O / ADE-A) had significant influence on hydrchar yield.
- Reaction time (t) was insignificant.
- Hydrchar yield decreased at higher T.
- ADE-A had lower hydrochar yield compared with ADE-O, as shown in Fig. 4, which is consistent with mass balance in Fig.1.

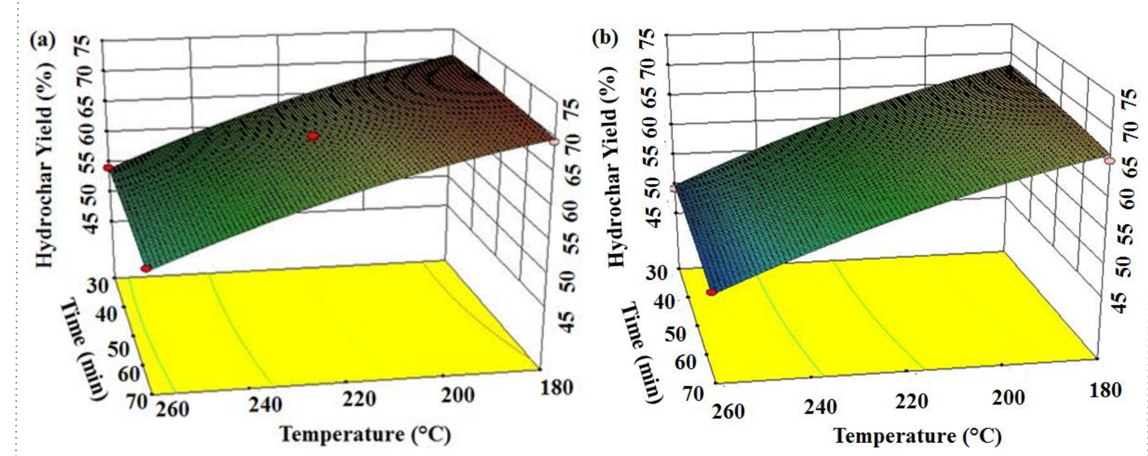

Fig 4. *Hydrochar yield of HTC (a) ADE-O; (b) ADE-A*

Energy yield

- For energy yield, it seemed that only T was significant, as shown in Fig. 5.
- The higher the temperature, the lower the energy yield.

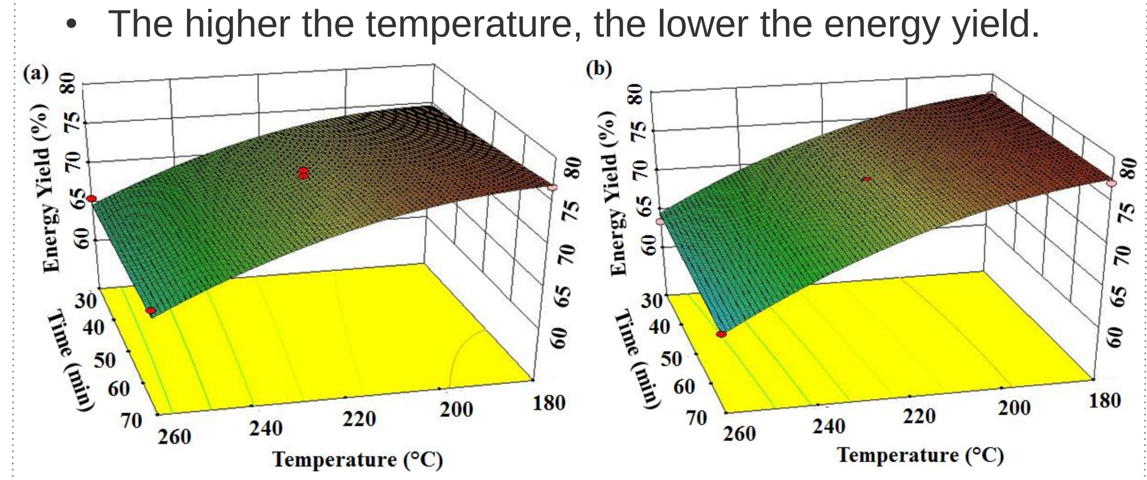

Fig 5. *Energy yield of HTC (a) ADE-O; (b) ADE-A*

Calorific value of biochar

- Both T and t had significant effects on the calorific value of biochar. When T and/or t increased, HHV increased, as shown in Fig. 6.
- When T ≥ 260°C, HHV of hydrochar was higher than 20 MJ/kg, which was the same level as coal used for electric, residential/ commercial utility[5].
- When trying to optimize parameters for the HTC process, to make the energy content in hydrochar applicable, HHV value was set to a point ≥ 20 MJ/kg. The energy yield and hydrochar yield should be as high as possible.

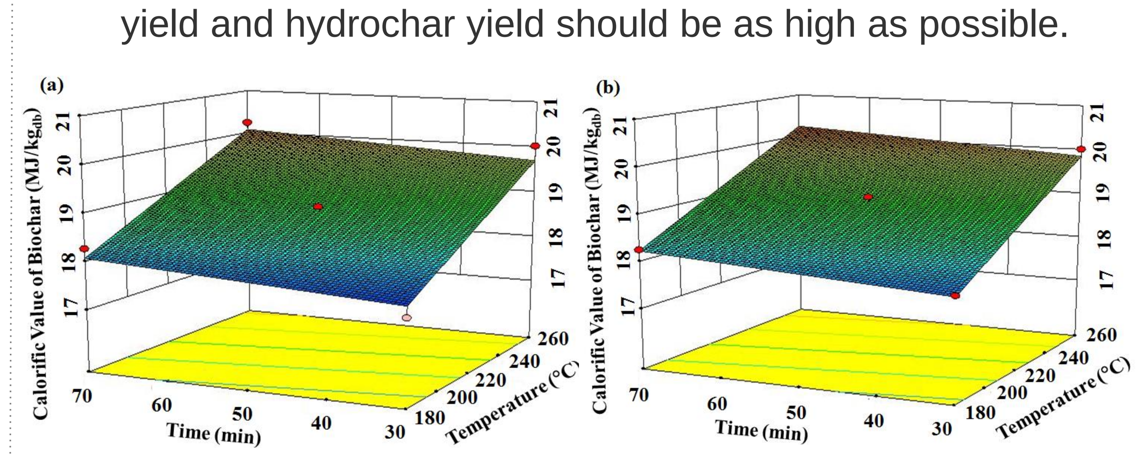

Fig 6. *Calorific value of biochar from HTC (a) ADE-O; (b) ADE-A*

Summary of the RSM model

- For optimization of hydrochar production, calorific value, energy yield and mass yield were comprehensively considered.
- The optimized HTC process was at 260°C, 70 min with ADE-A.
- All three models were significant with insignificant lack of fit, which means data were reliable and the models were good for prediction and optimization. Summary of models is shown in Table 1.
- Results from verification experiments were very close to the predicted results from model, providing an optimized solution for hydrochar production.

Table 1. *Summary of RSM models*

	Model type	Predicted results	Verification experiment results
Calorific Value	Linear	20.24 MJ/kg	20.18 MJ/kg
Energy yield	Quadratic	62.98%	62.99%
Hydrochar yield	Quadratic	48.78%	49.09%
Optimized combination：260°C，70 min with ADE-A			

COD analysis of liquid

- COD of HTC processed water was also investigated to gain primary insight of the possibility of liquid utilization. Results showed that more than 30% COD remained in the liquid (data not shown).
- Experiments for biogas potential (BMP test) of liquid should be further carried out for evaluation of the feasibility to integrate HTC after AD, in addition to the liquid from HTC going back to the AD digester.

CONCLUSIONS AND FURTURE WORKS

- Among the three parameters evaluated for the HTC process, temperature was the most significant.
- Optimization models set up for hydrochar production showed 260°C, 70 min with ADE-A was the best option. Hydrochar with calorific value about 20.18 MJ/kg could be achieved with mass and energy yields of 49.09% and 62.98%, respectively.
- Further BMP test of liquid will facilitated the evaluation of water recirculation to the AD system.

BIBLIOGRAPHY

1. Monlau, F., *et al*. 2015. Applied Energy, 148, 32-38.
2. Koottatep, T., *et al*. 2016. Renewable Energy, 99:978-985.
3. Lu, X., *et al*. 2014. Bioresource Technology, 166:120-131.
4. Basso, D., *et al*. 2016. Waster Management, 47: 114-121.
5. United States Environmental Protection Agency, Climate Leaders Greenhouse Gas Inventory Protocol Core Module Guidance Direct Emissions from Stationary Combustion Sources, May 2008. EPA430-K-08-003.

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